FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 251713

U.S. APPLN. NO. (If known, see 37 CFR 1.5): 09/913280

INTERNATIONAL APPLICATION NO.:	INTERNATIONAL FILING DATE:	PRIORITY DATE CLAIMED:
PCT/ZA00/00024	11 FEBRUARY 2000	11 FEBRUARY 1999

TITLE OF INVENTION: PROCESS FOR THE MANUFACTURE OF FURFURAL

APPLICANT(S) FOR DO/EO/US: Karl J. ZEITSCH

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   - a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   - b. [ ] has been transmitted by the International Bureau. (see attached copy of PCT/IB/308)
   - c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   - a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   - b. [ ] have been transmitted by the International Bureau.
   - c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   - d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Item 11. to 16. below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [ ] A **FIRST** preliminary amendment.
    [ ] A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT/IPEA/409), INTERNATIONAL SEARCH REPORT (PCT/ISA/210), ABSTRACT on a separate sheet, APPLICATION DATA SHEET

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/913280	INTERNATIONAL APPLICATION NO. PCT/ZA00/00024	ATTORNEY'S DOCKET NO. 251713

17. [X] The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR1.482) nor international search fee (37 CFR1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... $ 1,000.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... $ 860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... $ 710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... $ 690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... $ 100.00

	CALCULATIONS PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00
Surcharge of $130.00 for furnishing the oath or declaration later than 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$
Total claims	13 - 20 =	0	X $18.00	$
Independent claims	1 - 3 =	0	X $80.00	$
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)			+$270.00	$
			TOTAL OF ABOVE CALCULATIONS =	$ 990.00
Reduction of ½, if applicant is entitled to Small Entity status under 37 CFR 1.27.			+	$
			SUBTOTAL =	$ 990.00
Processing fee of $130 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR1.49(f)).				$
			TOTAL NATIONAL FEE =	$ 990.00
Fee for recording the enclosed assignment (37 CFR1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property			+	$
			TOTAL FEES ENCLOSED =	$ 990.00
			Amount to be refunded:	
			charged:	

a. [X] A check in the amount of $ **990.00** to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. **25-0120** in the amount of $ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required by 37 CFR 1.16 and 1.17, or credit any overpayment to Deposit Account No. **25-0120**. A duplicate copy of this sheet is enclosed.

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August 13, 2001

By Benoît Castel
Benoît Castel
Attorney for Applicant
Registration No. 35,041

Application Data Sheet

Application Information

Application Type::	Regular
Subject Matter::	Utility
Suggested Classification::	
Suggested Group Art Unit::	
CD-ROM or CD-R?::	None
Number of CD disks::	
Number of Copies of CDs::	
Sequence Submission?::	None
Computer Readable Form (CRF)::	No
Number of copies of CRF::	0
Title::	
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Request for Non-Publication?::	No
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Total Drawing Sheets::	
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Latin Name::	
Variety Denomination Name::	
Petition Included?::	No
Petition Type::	
Licensed US Gov't Agency::	
Contract or Grant Numbers::	
Secrecy Order in Parent Appl.?::	No

Applicant Information

Applicant Authority Type:: Legal Representative

Primary Citizenship Country::

Status:: Full Capacity

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1-11

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Correspondence Information

Correspondence Customer Number:: 000466

Representative Information

Representative Customer Number::	000466

Domestic Priority Information

Application::	Continuity Type::	Parent Application::	Parent Filing Date::

Foreign Priority Information

Country::	Application Number::	Filing Date::	Priority Claimed::

Assignment Information

Assignee Name::

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State or Province of Mailing Address::

Country of Mailing Address::

Postal or Zip Code of Mailing Address::

PROCESS FOR THE MANUFACTURE OF FURFURAL

TECHNICAL FIELD OF THE INVENTION

This invention relates to a process for the manufacture of furfural.

BACKGROUND OF THE INVENTION

Chemical reactors must be designed to suit the characteristics of the process intended. In making furfural, this has not been the case. For the first industrial production of furfural, QUAKER OATS used reactors from an abandoned cereal process as they happened to be available, and such reactors have been used ever since. Later, ROSENLEW and ESCHER WYSS built furfural plants based on reactors designed for making wood pulp. None of the industrial furfural reactors employed today were conceived to meet the special requirements of furfural production, and it is, therefore, not surprising that the yields obtained with these reactors do not even exceed 60%.

The principal yield losses are caused by a reaction between furfural and xylose, so that striving for a high yield forbids having furfural and xylose in the same place. All existing furfural reactors violate this requirement. By pointedly eliminating this deficiency, the process here described permits attaining yields in the order of 100%.

In analytical chemistry, the conversion of pentosan or pentose to furfural is used for a quantitative determination of these substances. This is possible as it was shown that in this procedure the furfural yield is a proven 100%. The procedure consists in an atmospheric digestion of pentosan or pentose in 12% aqueous HCl saturated with NaCl. By contrast, in the present industrial furfural processes mentioned above, a pressure reactor is used to submit the raw material to a steam treatment. By condensing, the steam effects heating to a constant temperature, and by passing through the raw material, it entrains furfural produced therefrom. The furfural reaction is catalysed either by added mineral acid or by various carboxylic acids (mainly acetic acid and formic acid) formed from the raw material. As compared to the analytical furfural process, a fundamental difference lies in the fact that in the latter process an appropriate heat input maintains the reaction medium in

a state of boiling, whereas in the industrial processes at any pressure a condensation of steam is thermodynamically incapable of bringing the reaction medium, a pentose solution, to boiling, because of the boiling point elevation caused by the xylose. The difference is illustrated schematically in Figure 1 showing phase diagrams for furfural in an aqueous solution boiling at 110°C (12% HCl saturated with NaCl), and in an aqueous solution boiling at 101°C (xylose solution). If a small furfural concentration ξ is generated in the first system representing the analytical furfural process, this leads to point A lying in the vapour field, which means that any furfural formed in this boiling solution will be instantly transformed to vapour where it cannot react with pentose as the latter is not volatile. Consequently, in this case, loss reactions between furfural and pentose are impossible, which explains the proven yield of 100%.

On the other hand, if a small furfural concentration ξ is generated in the second system, and if this system is heated by condensing steam at atmospheric pressure, this leads to point B lying in the liquid field. Hence, in the present industrial furfural reactors the reaction medium is not brought to boiling, so that the furfural remaining in solution can react with pentose to form furfural pentose, which explains the known high yield losses. The entrainment of furfural vapour by the steam flow does not change this statement to any significant extent, since this entrainment is a slow and inefficient process giving the loss reactions in the liquid phase plenty of time to take place.

As the principal difference between the analytical furfural process of 100% yield and the industrial processes of less than 60% yield lies in the fact that in the first case the reaction medium is boiling while in the second case it is not boiling, it was compelling to create an industrial process in which the reaction medium is maintaining in a state of boiling. In view of the fact that with giant furfural reactors, charged with solids not conductive to being stirred, an indirect energy input by heating the walls can be ruled out, it is the essence of this invention to bring about continuous boiling by a gradual (slow) depressurisation. In this fashion, a uniform boiling down to molecular dimensions is enforced without a need for mixing.

Apart from the poor yields achieved, the present commercial processes available are extremely expensive to operate. This is due to the large quantities of steam required,

typically 30 to 50 tons of steam per ton of furfural produced, and also the lengthy reaction times of between 2 and 5 hours.

It is therefore an object of this invention to provide a manufacturing process which not only produces a greater yield, but also requires a lower input of steam per ton of furfural produced and results in a shorter reaction time.

DISCLOSURE OF THE INVENTION

According to the invention, a process for the manufacture of furfural includes the steps of charging a reactor with a pentosan containing material, acidified or not, heating the charge by introduction of pressurised steam to a first predetermined temperature, closing the steam inlet valve of the reactor and subjecting the charge to a gradual reduction of pressure until a second predetermined temperature is attained, the depressurisation maintaining the liquid phase within the reactor in a constantly boiling state.

In the preferred form rate of depressurisaton is sufficient to complete the conversion to furfural before a second predetermined temperature is attained. Also in the preferred form of the invention, the charge is acidified prior to heating.

Also in the preferred form of the invention, the gradual depressurisation comprises the controlled leaking of a stream of vapour from the reactor until the second predetermined temperature is attained.

In one form of the invention, a first depressurisation is followed by a reheating to a temperature at or near the first predetermined temperature, the reheating being followed by a second gradual depressurisation.

Subsequent reheating and depressurisation cycles may also be employed if required.

In one form, steam may be added during depressurisation to increase the reaction temperature and improve yield.

In the preferred form of the invention, the charge material may be in solid or liquid form. Bagasse from sugar cane is a common feed and may be added to the reactor in solid or slurry form. Alternative feeds may include any other pentose-containing material, typical examples being corn cobs, bamboo, wood chips, olive press-cake amongst others.

Also in the preferred form of the invention the gradual depressurisation takes place in the temperature range between 280° Celsius and 150° Celsius, however the preferred range of operation is between 230° Celsius and 170° Celsius.

By an appropriate choice of the first and second temperatures, and by appropriate selection of a mineral or organic acid concentration, it is possible, if desired, to complete the process in a single depressurisation period since high temperatures and high acidity result in a short reaction time.

In the preferred form of the invention, phosphoric acid is used as the catalyst.

An apparatus for use in a process according to the invention comprises a pressure reactor including an inlet for steam under pressure, and an outlet for condensate vapour, the inlet and outlet including one or more valves for controlling the flow rate therethrough.

The outlet includes, after a valve, an orifice plate of predetermined dimensions for assisting in controlling the rate of depressurisation. In this form, the valve and orifice plate may be operated in tandem to obtain a range of depressurisation rates or a flow control valve governed by temperature or pressure can be used.

In any form of the invention the reactor may be thermally well insulated.

In an alternative form of the invention the reactor walls are designed to be heated. Also in this form, all valve operations are preferably controlled automatically by a computerised control unit. It has been demonstrated experimentally, on a pilot plant scale, that by maintaining the liquid phase of the reaction medium in a state of boiling throughout the reaction period, the furfural yield obtained is substantially greater than current

commercial processes, and if correctly controlled may approach yields achieved in the analytical furfural process. The Applicant contends further that apart from increasing the yield, the process of the invention is operable at substantially lowered capital and productions costs, for the following reasons:

(1), The process of the invention does not use steam for stripping furfural from the mass of feed material as once the reactor is sufficiently heated, the steam inlet is closed. Further steam will only be required briefly if a reheating cycle is employed.

(2), As a result of the non-use of steam to strip the furfural, the volume of condensate existing the reactor is significantly reduced and the concentration of furfural therein will be proportionately increased in relation to existing processes. This increased furfural concentration will greatly simplify the primary azeotropic distillation. In special cases, for instance in the application of the furfural as a nematicide, no distillation is needed at all.

(3), The product of the invention contains less acetic and formic acid (formed from the raw material) since, after reaching the second predetermined temperature of the decompression, most of these by-products are discharged with the residue. This greatly reduces the loading of the effluent generated by the plant.

DESCRIPTION OF THE INVENTION

The process according to the invention is described below with reference to Figure 2 which is a schematic diagram of the process and apparatus.

A thermally well insulated reactor 1 charged with raw material acidified or not, is heated to a temperature T_1 by admitting steam through valve 2 while the valves 3 and 4 are closed. During the very short heating process, the steam condenses, thus increasing the moisture content of the charge. Then, valve 2 is closed and a leak valve 3 is opened so as to produce a steady small flow of product vapour by gradual depressurisation. This causes a slow drop in temperature. When in this fashion a suitably chosen temperature T_2 is reached, the leak valve 3 is closed to terminate the first "gradual depressurisation". If at the end of this period no more furfural was obtained, the digestion is completed by opening

valve 4 to discharge the residue. If, however, furfural was still obtained, the reactor is reheated and submitted to another "gradual depressurisation" period. This procedure can be arbitrarily repeated. All valve operations are governed by an automatic control unit 5.

By an appropriate choice of the temperatures T_1 and T_2, and by an appropriate choice of the acid concentration, it is possible, if desired, to complete the process in a single depressurisation period since high temperature and high acidity permit a short reaction time.

Needless to say, designing such an operation is complicated as the furfural reaction takes place over a wide range of temperatures (e.g. from 230°C to 160°C), but once calculated, the practical realisation of the process is extremely simple.

As due to the continuous leak stream the reaction medium is maintained in a state of boiling throughout the reaction period, the furfural yield corresponds to that of the analytical furfural processes by lying in the order of 100%.

CLAIMS:

1. A process for the manufacture of furfural characterised in that the steps of charging a reactor with pentosan containing material, heating the charge by introduction of pressurised steam to a first predetermined temperature closing the inlet valve of the reactor, and subjecting the charge to a gradual reduction of pressure until a second predetermined temperature is attained, the depressurisation being at a rate sufficient to maintain the liquid phase within the reactor in a constantly ebullient state.

2. A process according to claim 1 characterised in that the charge is acidified prior to heating.

3. A process according to claim 1 characterised in that the rate of depressurisation is sufficient to complete conversion to furfural before the second predetermined temperature is reached.

4. A process according to claim 1 characterised in that the complete conversion to furfural is obtained in more than one depressurisation from the first predetermined temperature to the second predetermined temperature by the addition of steam.

5. A process according to claim 1 characterised in that steam is added during the depressurisation, for a predetermined period.

6. A process according to claim 1 characterised in that the gradual depressurisation comprises the controlled leaking of a stream of vapour from the reaction until the second predetermined temperature is attained.

7. A process according to claim 1 characterised in that the gradual depressurisation takes place in the temperature range between 280° Celsius and 150° Celsius.

8. A process according to claim 7 characterised in that the temperature range of operation is between 230° Celsius and 170° Celsius.

9. A process according to claim 1 characterised in that phosphoric acid is used as the catalyst.

10. A process according to claim 1 characterised in that acetic acid is used as the added catalyst.

11. An apparatus for the manufacture of furfural according to the process of claim 1 characterised in that it comprises a pressure reactor including an inlet for steam under pressure comprising one or more valves, and an outlet comprising a flow control valve or the combination of a shut-off valve and an orifice of predetermined dimensions.

12. An apparatus according to claim 11 characterised in that the reactor is thermally well insulated.

13. An apparatus according to claim 12 characterised in that the wall of the reactor is adapted to be heated and/or heat exchange surfaces are incorporated inside the reactor.

ABSTRACT OF THE DISCLOSURE

Process for the manufacture of furfural wherein a pentosan-containing raw material acidified or not, is heated to a temperature T_1 by admitting steam through valve 2 while the valves 3 and 4 are closed. During the very short heating process, the steam condenses, thus increasing the moisture content of the charge. Then, valve 2 is closed and a leak valve 3 is opened so as to produce a steady small flow of product vapor by gradual depressurization. This causes a slow drop in temperature. When a suitably chosen temperature T_2 is reached, the leak valve 3 is closed to terminate the first "gradual depressurization". If at the end of this period no more furfural was obtained, the digestion is completed by opening valve 4 to discharge the residue. If, however, furfural was still obtained, the reactor is reheated and submitted to another "gradual depressurization" period.

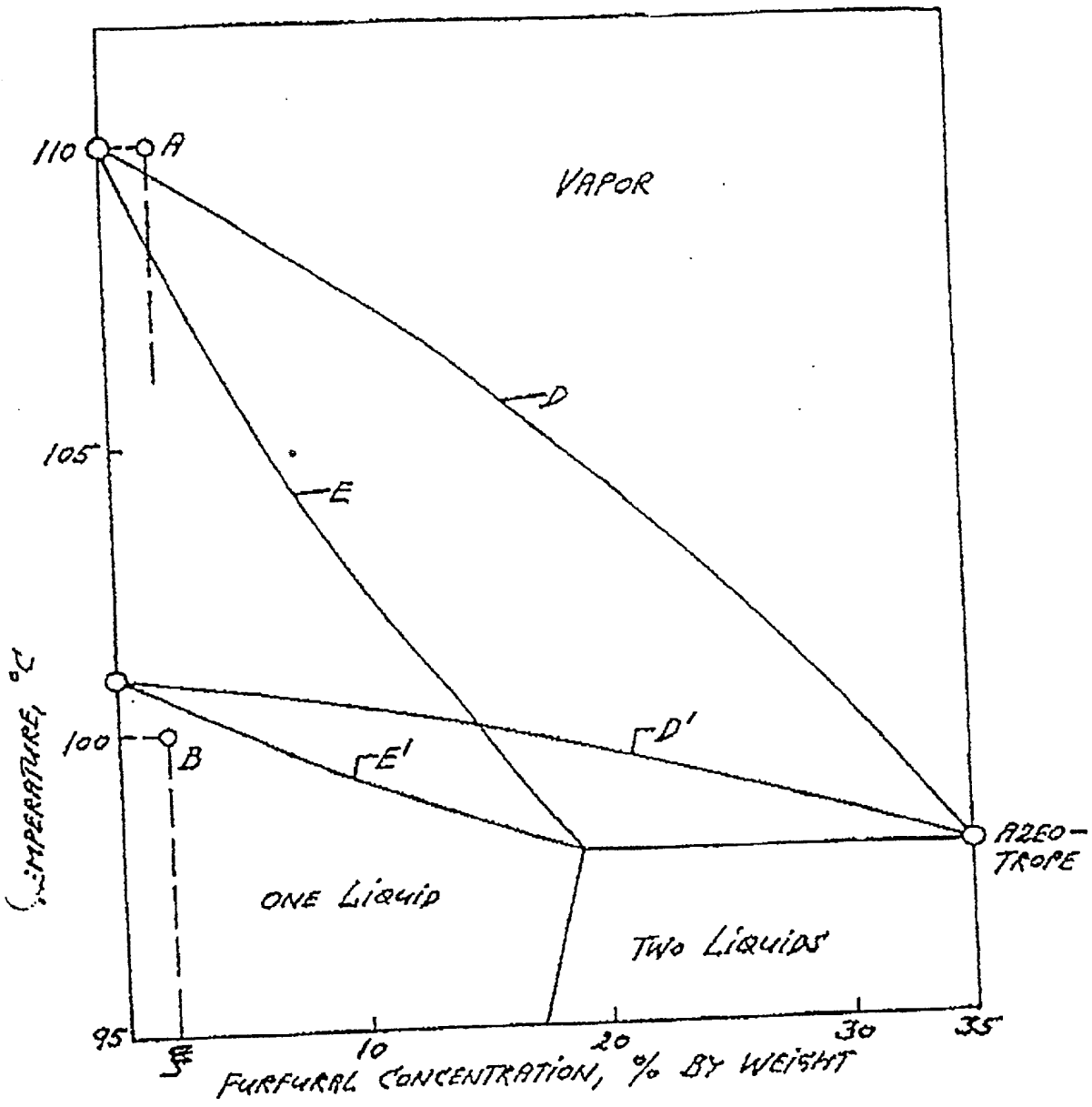

Figure 1. Phase diagram for explaining the difference between analytical and industrial furfural processes.

D and D': Dew point curves

E and E': Boiling point curves

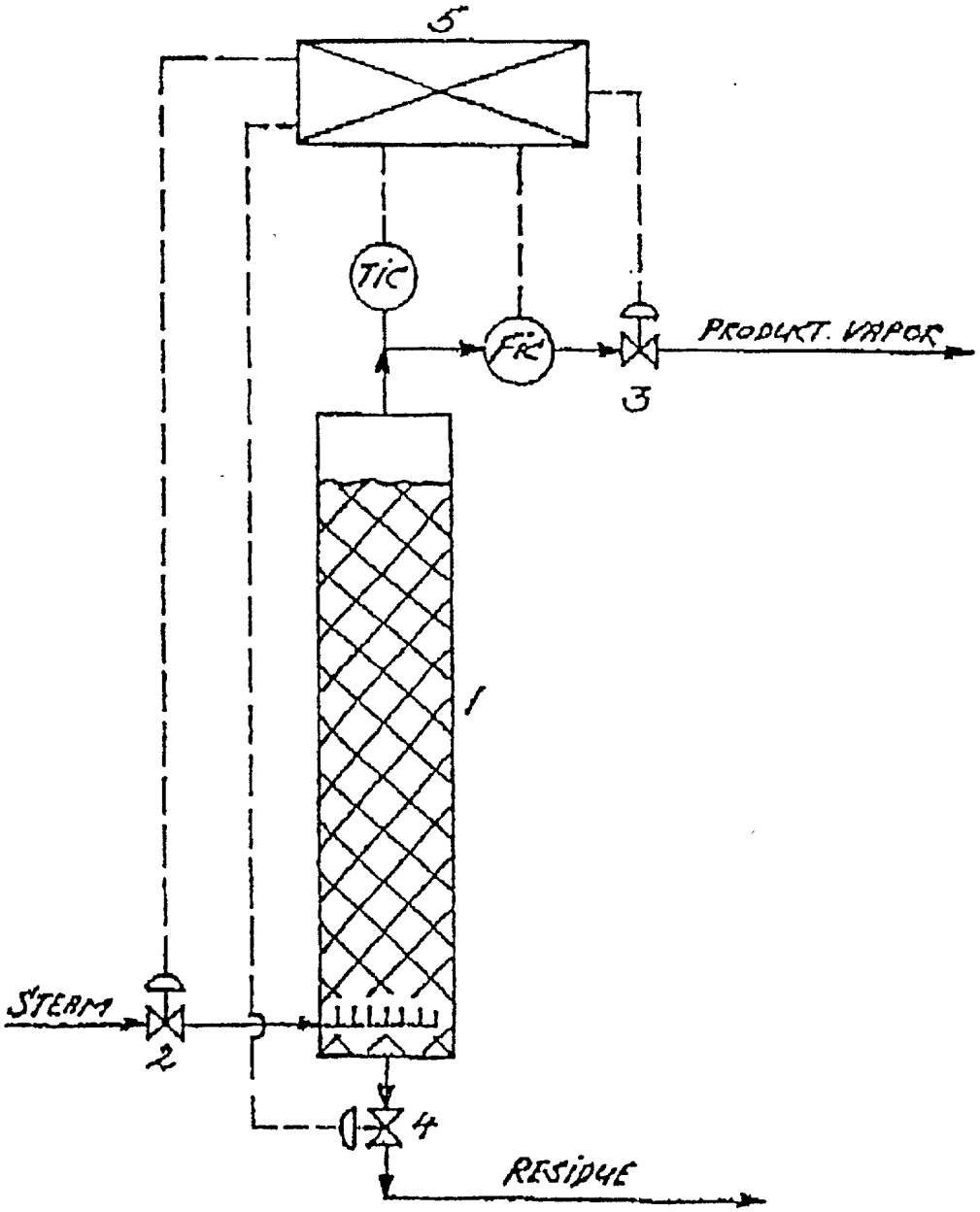

Figure 2 Schematic of the delayed decompression process for the production of furfural.

251713

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS FOR THE MANUFACTURE OF FURFURAL

the specification of which: *(check one)*

REGULAR OR DESIGN APPLICATION

[ ] is attached hereto.

[X] was filed on **August 13, 2001** as application Serial No. **09/913,280** and was amended on _____ (if applicable).

PCT FILED APPLICATION ENTERING NATIONAL STAGE

[X] was described and claimed in International application No. **PCT/ZA00/00024** filed on **11 February 2000**, and as amended on _____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

PRIORITY CLAIM

I hereby claim foreign priority benefits under 35 USC 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)

Country	Application Number	Date of Filing (day, month, year)	Priority Claimed
Germany	199 05 655.2	11 February 1999	Yes

(Complete this part only if this is a continuing application.)

I hereby claim the benefit under 35 USC 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 35 USC 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.) (Filing Date) (Status--patented, pending, abandoned)

POWER OF ATTORNEY

The undersigned hereby authorizes the U.S. attorney or agent named herein to accept and follow instructions from Morrison Forster, Inc. as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney or agent named herein will be so notified by the undersigned.

As a named inventor, I hereby appoint the registered patent attorneys represented by Customer No. 000466 to prosecute this application and transact all business in the Patent and Trademark Office connected therewith, including: Robert J. PATCH, Reg. No. 17,355, Andrew J. PATCH, Reg. No. 32,925, Robert F. HARGEST, Reg. No. 25,590, Benoit CASTEL, Reg. No. 35,041, Thomas W. PERKINS, Reg. No. 33,027, and Roland E. LONG, Jr., Reg. No. 41,949 and Eric JENSEN, Reg. No. 37,855,

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-01 Full name of sole or first inventor: Karl J. ZEITSCH (Deceased)
(given name, family name)

Inventor's signature ______________________ Date ______________

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1-11 I, Hanna TEPOHL, hereby declare that, I am a citizen of Germany, residing at 50931 Köln Classen-Kappelmann Str. 35-41, that I am executing and signing this declaration as legal representative of the Inventor, Karl J. ZEITSCH (deceased).

That, upon information and belief, I aver those facts which the inventor is required to state.

Köln, den 27.2.02 [signature]
Date Hanna TEPOHL, LEGAL REPRESENTATIVE OF KARL J. ZEITSCH